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SiCO ceramic microspheres produced by emulsion processing and pyrolysis of polysiloxanes of various structures

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ABSTRACT

Crack-free silicon oxycarbide microspheres were synthesized from precursors obtained by a one-pot aqueous emulsion-process of modified polyhydromethylsiloxane. The process involved cross-linking by hydrosilylation and the advanced hydrolysis of polyhydromethylsiloxane SiH groups to SiOH. These species then participate in SiOH+SiH condensation, enhancing the cross-linking. The microspheres were additionally modified by SiH group-substitution in the initial polymer and by using various cross-linkers. The precursor powder particle structure was also modified by varying the stirring rate during emulsification. The modified preceramic microspheres, with average diameters from 7.6 to 56 μm, were subjected to pyrolytic processes at various temperatures. The chemical composition of the pyrolyzed microspheres and their precursors was studied by ^{29}Si and ^{13}C MAS NMR, FTIR spectroscopy, and elemental analysis. The structures of the microspheres were examined by SEM. Selected samples were also investigated by XRD and Raman spectroscopy. All of the synthesized preceramic microspheres retained their regular spherical shapes during pyrolysis at temperatures of up to 1200 °C. Heating at 1000 °C and 1200 °C yielded amorphous silicon oxycarbide ceramic materials with segregated free carbon domains. The chemical structure and morphology of the obtained ceramic microspheres were significantly influenced by the modification of the preceramic materials.

1. Introduction

The development of polymer-derived ceramics (PDCs) opens the possibility of the easy generation of ternary silicon oxycarbide (SiCO) ceramic materials, which are known for their excellent oxidation and creep resistance as well as their chemical and thermal stability [1–3]. PDC pathways have also allowed for the preparation of SiCO ceramic powders with controlled purity and structure. Among these, SiCO microspheres, spherical particles with diameters ranging from 0.1 to 100 μm, have been prepared [4–12]. Interest in these particles comes from their great application potential in many areas of technology, science and medicine [1,2]. They can be used for the preparation of ceramic materials by powder sintering processes [1,10,12,13] and as fillers preventing the formation of pores and cracks in PDCs [1,2,14]. The SiCO microspheres are also good candidates for carriers of high temperature reaction catalysts [15,16], sensors [17], and anodes of lithium batteries [18,19], as well as precursors for supercapacitors and absorbers [20]. The biocompatibility of SiCO leads to a variety of possible medical applications of these materials [21,22].

The chemical composition and morphology of PDCs is highly dependent on their precursors. SiCO microspheres are usually prepared by the ceramization of commercial silicone resins [7,8,10] or polymers obtained by sol-gel techniques [5,9]. These precursors are mostly built of silsesquioxane cages and ladders, which give them a rigid structure, resulting in cracking of the material during pyrolysis [10]. We believe that polysiloxane networks obtained by cross-linking of linear, flexible polymers are better precursors for generating crack-free microspheres. Recently, we developed a method that is suitable for the synthesis of polysiloxane microspheres containing a large number of reactive SiOH and SiH groups [23]. The method is based on processing in an emulsion of polyhydromethylsiloxane modified by vinylsiloxane groups grafted to the polymer chains. Cross-linking of the polymer by hydrosilylation catalyzed by a Pt(0) complex, carried out in the emulsion, is accompanied by the hydrolysis of SiH groups to silanol and by the condensation of the latter with the SiH groups. Both reactions are catalyzed by the same Pt(0) complex. Microspheres formed by this method are composed of polysiloxane chains that are cross-linked by two types of bridges: flexible ones

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($\equiv$SiOSiCH$_2$CH$_2$SiOSi$\equiv$) formed by hydrosilylation and more rigid ones formed by condensation ($\equiv$SiOSi$\equiv$). Because of their large number of silanol groups, the microspheres are hydrophilic [24,25]. Recently, we demonstrated that these particles are very attractive as precursors of ceramic microspheres because their loose and flexible structure allows them to retain their spherical shape during heating [4]. Moreover, the ceramization process involving cross-linked microspheres does not require a preliminary cross-linking step. Condensation of silanol groups during heating produces additional bridges between polymer chains. The presence of these bridges suppresses polysiloxane depolymerization.

Our synthetic method provides many possibilities for in-situ modification of the polysiloxane microspheres. The modification consists in introducing various substituents to the precursor polysiloxane chains by using the SiH groups of the polymer in the alcoholysis or hydrosilylation reactions. Both of these reactions are promoted by the same Pt(0) catalyst used in the cross-linking and silanol formation during the emulsion processing of the microspheres. Another method to modify the microspheres uses various olefin-containing cross-linking agents. The goal of this study is to determine how the chemical structure and morphology of the polysiloxane microspheres pyrolyzed at various temperatures may be altered by these modification methods. Our goal was to show that these modifications would not adversely affect the formation of powders consisting of crack-free ceramic microspheres and that this approach would yield structural tuning methods for these particles.

2. Experimental

2.1. Materials

Polyhydromethylsiloxane (PHMS) terminated by trimethylsiloxy groups at both ends was purchased from ABCR as HMS 991 (M_n=3.6 *k*D as measured by ^{29}Si NMR). 1,3-Divinyltetramethyldisiloxane (DVTMDS) (97%) was also purchased from ABCR. 1,3,5,7-Tetravinyltetramethylcyclotetrasiloxane (V$_4$) was prepared by hydrolytic condensation of methylvinyldichlorosilane with a purity $>99\%$, as determined by gas chromatography (GC). Divinylbenzene (DVB) isomers (80%, from the intensity of GC peaks: 55/25% of para/meta DVB mixture and 11/9% para/meta ethylstyrene), styrene (purity $\geq 99\%$) and isopropanol (CHEMPUR 99.7%) were purchased from Aldrich and used without additional purification, with their initial purity verified by GC. Poly(vinylalcohol) (PVA) was the product of POCH Gliwice (M_n=72 kD, purity 99.5%), and the Pt(0) Karstedt complex in a silicone oil solution containing 20 w/w% Pt was kindly donated by Momentive Performance GmbH Leverkusen.

2.2. Analytical methods

^{29}Si MAS NMR spectra were recorded using a DSX 400 Bruker spectrometer. The spectra of native microspheres and those heated at 400 °C and 600 °C were recorded with cross-polarization, applying 90-ms pulses with a 6-s pulse delay and a 3-ms contact time, for samples in a 4.0-mm zirconium rotor spinning at 8 kHz and the peak position referenced to Q$_8$M$_8$. The integral peak areas corrected to those obtained with a single pulse excitation using the high power decoupling mode (HPDec) spectra (90 pulse of 5 µs, relaxation delay 100 s) taken for selected samples. The spectra of samples heated at 1000 °C and 1200 °C were acquired in the HPDec mode with 90 pulses and a 60–100 s relaxation delay. ^{13}C HPDec MAS NMR spectra were taken using a DSX 400 Bruker spectrometer with a repetition delay of 60 s for samples heated at 600 °C, 1000 °C and 1200 °C. FTIR spectra were recorded using a Bruker 70 V spectrometer at a resolution of 4 cm^{-1} after the accumulation of 128 scans. The standard KBr pellet technique was used in transmission mode, whereas ATR spectra were measured using a ZnSe crystal and a beam angle of 45°. TGA analyses were performed using a TA Instruments 2950 TGAHR Analyzer with a heating rate 10 °C/min. Raman spectra were taken using a Ramana HORIBA LabRAM HR microspectrometer using a λ_{exc}=532.0 nm excitation beam emitted by a Nd-YAG laser. A 50x objective and 1800 g/mm grating were used. The acquisition time was set to 1200 s, and 2 scans were accumulated. X-ray diffraction was performed using a Panalytical X'Pert Pro MPD instrument equipped with a roentgen lamp with a copper anode, X'Celerator detector and Johansson monochromator. Measurements were carried out in Bragg-Brentano geometry in the range of 2θ from 5° to 75° with a 0.008° step and step time of 106 s Elemental analysis was performed for carbon and hydrogen using an automatic EuroVector model 3018 analyzer. SEM images were recorded using a Jeol JSH 5500 LV microscope in high vacuum mode at an accelerated voltage of 10 kV. Samples were coated with a fine layer of gold (approximately 20 µm thick) using an ion coating JEOL JFC 1200 apparatus. The size distribution and average diameter of the microspheres were calculated from SEM images by counting the diameters of one thousand particles in a random sample using a SigmaScan program.

2.3. Preparation of polysiloxane preceramic microspheres

Synthesis of unmodified microspheres: Preceramic (native) polysiloxane microspheres containing a large number of SiOH groups cross-linked by the hydrosilylation of 1,3-divinyltetramethyldisiloxane (DVTMDS) were prepared in a two-step one pot synthesis. In the first step, PHMS was modified by grafting vinyl groups, followed by an emulsion process in which the PHMS was solidified via polymer cross-linking in parallel with the formation of many silanol groups as described previously [4]. A significantly lower conversion of SiH groups in PHMS into SiOH groups and a lower average microsphere size was attained by modifying the emulsification procedure (homogenization at a very high rotor speed, 30,000 rpm, using a CAT Unidrive x1000 homogenizer).

Synthesis of microspheres cross-linked by DVB and V$_4$: Native polysiloxane microspheres cross-linked by hydrosilylation of divinylbenzene (DVB) or 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane (V$_4$) were prepared similarly to those cross-linked by DVTMDS. An example of the synthesis is presented below.

PHMS (48.0 g) containing 0.76 mol of SiH was mixed with DVB (7.68 g, 0.059 mol) in 40 mL of dioxane and then warmed to 45 °C, and 0.24 mL of the dioxane solution of the Karstedt catalyst containing 6.1×10^{-3} g (3.2×10^{-5} mol) of Pt was introduced. The solution was stirred for 4 min and then homogenized for 2.5 min at 45 °C and 7500 rpm using a MPW-120 homogenizer with a solution of 2.25 g of PVA (poly(vinyl alcohol)) in 600 mL of distilled water. The emulsion was diluted with a solution of 9.75 g of PVA in 2600 mL of degassed water at 45 °C. It was stirred at this temperature for 90 h and left for 18 h to allow microsphere sedimentation. Isolated microspheres were repeatedly rinsed with water and centrifuged. They were then freeze-dried and analyzed. A total yield of 46.6 g (75.5% yield) of dry microspheres was obtained. A 9.8 g fraction of small microspheres that did not sediment out was regained from the supernatant, giving a total microsphere yield of 91.3%.

Synthesis of microspheres partly substituted with 2-phenylethyl groups: PHMS (48.0 g) containing 0.764 mol of SiH groups was mixed with 24.8 g (0.238 mol) of styrene and 1.2 mL of undecane, which was used as a GC standard. The mixture was set at 45 °C, and 0.04 mL of the Karstedt catalyst solution (containing 0.0254 g of catalyst in 1 mL of dioxane) was introduced. The conversion of styrene was monitored by GC analysis of withdrawn samples. After 22 h, when the styrene conversion reached 98%, a